TABLE 2. Enthalpies of decomposition of THF hydrate

| Decomposition | Temperature (°C) | $\Delta H$ (kcal/mol) |
|---|---|---|
| $h \to l$ | 4.4 | $16.7 \pm 1.9$ |
| $h \to l_1 + l_2$ | 4.4 | $19.5 \pm 2.0$ |
| $h \to l_1 + g$ | 4.4 | $27.1 \pm 2.0$ |
| $h \to l_1 + g$ | 0 | $26.5 \pm 2.1$ |
| $h \to I + g$ | 0 | $2.1 \pm 2.1$ |

given by eq. 3. With $\Delta V(h \to l) = -5.8 \pm 0.3$ cm$^3$, $\Delta H(h \to l) = 16.7 \pm 1.9$ kcal/mol, at about the 95% confidence level.

We have crudely measured the heat of mixing of 1 mol of THF and 17 mol of water at a mean temperature of 4 °C, and found $\Delta H(l_1 + l_2 \to l) = -2.8 \pm 0.2$ kcal. This value is consistent with values read from Erva's figure (21), viz., $-2.25$ and $-2.60$ kcal for mixing at 25 and 15 °C, respectively. The heat of vaporization of liquid THF at 4.4 °C is found from the vapor pressure equation (22) to be $\Delta H(l_2 \to g) = 7.6 \pm 0.1$ kcal/mol. These quantities, together with estimates of specific heats between 4.4 and 0 °C, give the enthalpy changes shown in Table 2.

## Discussion

### Chloroform Hydrate

The only comparable study of the volume change of decomposition of a structure II hydrate appears to be that of Tammann and Krige (23), who measured the volume change and temperature of decomposition of chloroform hydrate to the sparingly miscible liquids at pressures to 2 kbar. Analysis of their data gives, with $\sigma = 0.00144$ cm$^3$/g,

[11]
$$\Delta v = (0.01956 \pm 0.00174)$$
$$- (5.547 \pm 0.470) \times 10^{-5} P$$
$$+ (1.0353 \pm 0.2476) \times 10^{-8} P^2$$

for the change in volume per gram of hydrate. These volume changes were measured indirectly from the changes of pressure at decomposition and were corrected (23) for the considerable amounts of excess water present. From eq. 11, $\Delta V(h \to l_1 + l_2)$ per mol of hydrate at 1 bar (and about 2 °C) may be written as a function of $n$.

The solubility at 2 °C of chloroform in water is only 0.96 and of water in chloroform only 0.02 weight % (24). Little error is introduced by assuming additivity of molar volumes in these dilute solutions:

[8′]
$$V(l_1 + l_2) = \frac{119.39}{1.5222} + \frac{18.015n}{0.999947}$$

where the density of chloroform is from Timmermans (25). $V(h)$ is given by eq. 9 with $a = 17.33 \pm 0.10$ Å (26).

The volume differences for chloroform hydrate are shown in Fig. 7. The uncertainty shown for $\Delta V(h \to l_1 + l_2)$ is double the standard error of the constant term in eq. 11.

The most probable value of $n$ is 17.25, but a value as high as 19.0 cannot be definitely excluded because of the large uncertainty of the lattice parameter. Conversely, if, as there is good reason to assume (see below), the large cages are at least 98% occupied, the value of $a$ is defined between 17.30 and 17.37 Å.

The pressure-dependence of the decomposition temperature of chloroform hydrate was not measured (23) with sufficient accuracy to permit a useful estimation of $\Delta H(h \to l_1 + l_2)$ from eq. 10. This quantity was found to be 22.9 kcal/mol by a calorimetric study made in 1885 (27). Addition of the heat of vaporization of chloroform at 2 °C gives $\Delta H(h \to l_1 + g) \simeq 30.7$ kcal/mol.

### Critical Decomposition Temperatures of Structure II Hydrates

For THF and chloroform hydrates the decomposition temperature is highest in the absence of externally-applied pressure. The melting tempera-
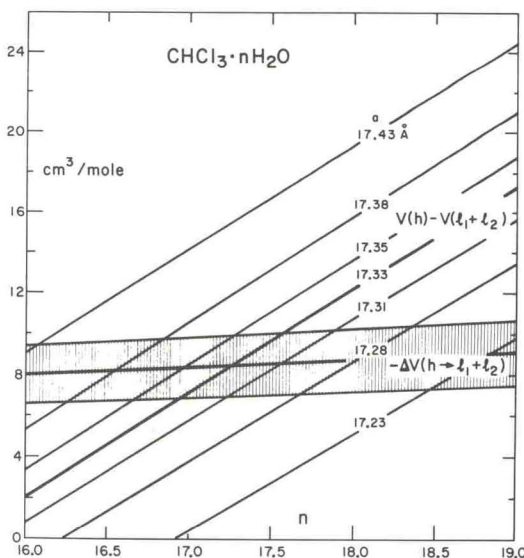


FIG. 7. Dependence of volume change at decomposition on composition of chloroform hydrate.

TABLE 3.   Composition of structure II hydrates*

| Hydrate | $\Delta H_1$ (h → $l_1$ + g) (kcal/mol) | $\Delta H_2$ (h → I + g) (kcal/mol) | From $\Delta H_1 - \Delta H_2$ | | From effect of NaCl | | Direct analysis |
|---|---|---|---|---|---|---|---|
| | | | $n$ | $w$ | $n$ | $w$ | $n$ |
| $SF_6$ | 29.57 | 5.14 | 17.02(33) | 3 | | | |
| Cyclopropane | 29.2 | 6.42 | 15.87(34) | 1 | 17.05(34) | 3 | |
| (Deuterate) | 32.37 | 6.44 | 17.18(35)† | 3 | | | |
| $n$-Propane | 32.1 | 6.34 | 17.94(36) | 1 | 17.9 (37) | 1 | 19.7(38) |
| Isobutane | 30.5 | 5.45 | 17.45(39) | 2 | 17.50(39) | 2 | 17.1(40) |
| $CH_3I$ | 31.4 | 7.3 | 16.79(13) | 1 | | | |
| $CHCl_3$ | 30.7‡ | | 17.25§ | 1 | | | 18 (27) 17.7(31) |
| $CHCl_2F$ | 32.72 | 8.51 | 16.86(41) | 2 | 16.80(42) | 2 | |
| $CCl_3F$ | 35.45 | 11.57 | 16.63(42) | 0 | | | |
| $CCl_2F_2$ | 30.14 | 7.79 | 15.57(42) | 0 | | | |
| $CBrClF_2$ | 32.567 31.86(43) | 8.254 | 16.94(29) | 4 | 16.57(43) | 2 | |
| $CBrF_3$ | 29.42 | 6.99 | 15.62(42) | 0 | | | |
| $CH_3CH_2Cl$ | 31.9 | 8.7 | 16.16(13) | 1 | | | |
| $CH_3CClF_2$ | 31.11 | 7.49 | 16.45(44) | 1 | 17.18(44) | 2 | |
| $C_4H_8O$ | 27.1‡ | | 16.86§ | 3 | | | |

*Reference numbers in parentheses.
†Based on heat of fusion of $D_2O$ of 1515 cal/mol.
‡Indirect value (see text).
§Present result from the density measurement method.

ture measured under the saturated vapor pressure of the hydrate is therefore a true "critical decomposition temperature", a result probably generally true of all simple structure II hydrates which decompose to give liquids. On the other hand, acetone hydrate decomposes to ice (and relatively acetone-rich liquid) at its incongruent melting point (8), which may be expected to rise somewhat with the application of pressure.

*Compositions of Structure II Hydrates*

Table 3 gives the results of earlier composition studies of structure II hydrates. The second and third columns show, respectively, the molar heats of decomposition into liquid water and gaseous hydrate-former and into ice I and gaseous hydrate-former, as derived from the dependence of pressure on temperature along the respective three-phase equilibrium lines. The difference between these heats at 0 °C is $n\Delta H(I \rightarrow l_1)$ (28). The value $n$ so obtained, with the heat of fusion of ice taken as 1435.7 cal/mol, is given in column 4. These values of $n$ vary greatly in accuracy, not only with the number and accuracy of the original data, but also with the adequacy of the corrections made for gas imperfection, the presence of water vapor in the gas, and the effect of finite solubility of hydrate-former in water. Only Glew (29) appears to have combined accurate measurements with a proper statistical

study of the errors. We have attempted to represent the relative accuracy of individual values of $n$ in terms of weights ($w$) assigned on a scale of 0 to 4.

Values of $n$ in column 6 were derived from the shift of the h–$l_1$–g equilibrium produced by addition of NaCl, according to the method of Miller and Strong (30). The values in the final column are the results of various attempts at direct analysis and are generally of lower accuracy. An exception is the analysis of chloroform hydrate by Barrer and Ruzicka (31) who found the large cages to be 94 to 98% occupied by chloroform with measurements made in the presence of various "help gases".

Consideration of these results suggests that in no case has a statistically significant departure from the ideal composition of $n = 17$ been demonstrated. Certainly this is true of the results as a whole. With cases of $w = 0$ omitted, the unweighted mean of the values of $n$ in columns 4 and 6 is $16.99 \pm 0.54$. More realistically, weighting according to $w^2$ gives $17.01 \pm 0.31$. Thus at about the 85% level of confidence, more than 98% of the large cages are occupied.

We conclude that the available composition data for structure II hydrates are of insufficient accuracy to test the extent of applicability of the relation between the μ-potential of water in equilibrium with the clathrate ($\mu_1$) and that of